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Kinetics of absorption of carbon dioxide in aqueous ammonia solutions

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Abstract

In the present work the absorption of carbon dioxide into aqueous ammonia solutions has been studied in a stirred cell reactor, at low temperatures and ammonia concentrations ranging from 0.1 to about 7 kmolm⁻³. The absorption experiments were carried out at conditions where the so-called pseudo first order mass transfer regime was obeyed – and hence the kinetics of the reaction between carbon dioxide and ammonia could be derived. The results were interpreted according to the well-established zwitterion mechanism.

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Keywords: Carbon dioxide ; ammonia ; kinetics ; absorption ; reaction mechanism

1. Introduction

Post combustion capture (PCC) with aqueous (alkanol)amine solutions is currently regarded as the most mature and feasible technology to reduce the carbon dioxide emissions from coal and natural gas fired power plants. In this capture process, usually the flue gas is countercurrently contacted in an absorber column, where the carbon dioxide reacts selectively with the solvent. The cleaned gas leaves the absorber top, while the loaded solvent is sent to a desorber, where it is regenerated at higher temperature, after which it is sent back to the absorber. The carbon dioxide leaving the desorber top is to be compressed and stored at a suitable location.

The major part of research within PCC is focused on solvent development, as the current ‘base case solvent’, an aqueous ethanolamine (MEA) solution, suffers from severe drawbacks: Degradation and corrosion issues and the relatively high heat of regeneration required in the stripper section are valid reasons to search for a more attractive solvent to be used in the post combustion capture technology.

The so-called “chilled ammonia” process, which has gained a lot of interest recently, is a post combustion

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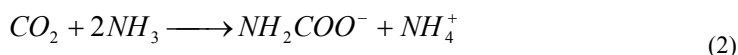
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technology based on a new solvent. In this process, the carbon dioxide is absorbed in an aqueous $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system, at temperatures between 0 and 10 °C [1]. Indispensable for an optimal design and operation of absorber and stripper is detailed knowledge on mass transfer and kinetics on one hand and thermodynamic equilibrium on the other hand. Several studies have been reported in the open literature dealing with the thermodynamic vapor-liquid(-solid) equilibrium in the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system [e.g. 2,3,4]. Unfortunately, relatively few studies have actually focused on the elemental kinetics of the individual reactions that occur when carbon dioxide is absorbed in aqueous ammonia based solvents [5,6]. The focus in the literature seems to lie on the determination of the more macroscopic potential of aqueous ammonia based solvents, such as e.g. its cyclic capacity and removal efficiency in bubble columns [e.g. 7,8]. The impact of the reaction kinetics on the process performance seems less important at this stage.

In this work, the kinetics of the reaction between ammonia and carbon dioxide in aqueous solutions are studied at temperatures between 5 and 25 °C; both the kinetic rate and the mechanism of the reaction are reported and discussed.

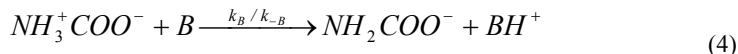
2. Kinetics

When carbon dioxide is absorbed in aqueous ammonia, its overall reaction rate will be determined by the following two reactions:



The aim of this study is to identify the reaction mechanism and kinetic rate constant of reaction (2). Depending on the order of magnitude of this reaction, a correction for the contribution of reaction (1) might be necessary.

The reaction between ammonia and carbon dioxide is, similarly to the reaction between CO_2 and primary and secondary alkanolamines, expected to proceed via the well-known zwitter-ion mechanism [9,10]. In a first reaction step (3), carbon dioxide reacts with ammonia to form a zwitterion, which is deprotonated in the second step (4) by any base present in solution (e.g. NH_3 or H_2O).



The overall rate equation is then given by equation (5) :

$$r_{\text{CO}_2\text{-NH}_3} = \frac{C_{\text{NH}_3} C_{\text{CO}_2}}{\frac{1}{k_2} + \frac{k_{-1}}{k_2} \frac{1}{\sum k_B C_B}} \quad (5)$$

The theory and the experimental procedures used in the experimental determination of the reaction rate will be described in the following two subsections.

3. Mass Transfer

The absorption rate of CO₂ into a lean, freshly prepared, (reactive) solution is generally described using equation 6:

$$J_{CO_2} = k_L E \frac{mP_{CO_2}}{RT} \quad (6)$$

where J_{CO_2} is the absorption rate (in mol m⁻² s⁻¹), k_L the physical liquid-side mass transfer coefficient (in m s⁻¹), E the enhancement factor for chemical reaction, m the distribution coefficient ($m = C_L / C_G$) and P/RT the gas phase CO₂ concentration (in mol m⁻³).

In case the absorption occurs in the so-called pseudo-first-order regime, the enhancement factor equals the Hatta number:

$$E = Ha = \frac{\sqrt{k_{OV} D_{CO_2}}}{k_L} \quad (7)$$

where D_{CO_2} is the diffusion coefficient of CO₂ in the solution (in m² s⁻¹). The overall kinetic rate constant k_{OV} is defined by:

$$k_{OV} = k_{OH} C_{OH} + \frac{r_{CO_2-NH_3}}{C_{CO_2}} \quad (8)$$

The kinetic rate constant of reaction (1), k_{OH} , is known in literature, while the hydroxide concentration can be estimated using the pKa of ammonia and the concentration used in the absorption rate experiment.

N.B. The criterion to ensure pseudo-first-order behaviour is:

$$3 < Ha \ll E_{inf} \quad (9)$$

where E_{inf} is the infinite enhancement factor:

$$E_{inf} = 1 + \frac{D_{NH_3}}{D_{CO_2}} \frac{C_{NH_3}}{\nu_{NH_3}} \frac{RT}{mP_{CO_2}} \quad (10)$$

4. Experimental

All absorption experiments were carried out in a thermostatted stirred-cell type of reactor equipped with both a pressure transducer and a thermocouple. Also, the reactor was connected to two gas supply vessels filled with either carbon dioxide or nitrous oxide. A schematic drawing of the experimental setup is shown in Figure 1.

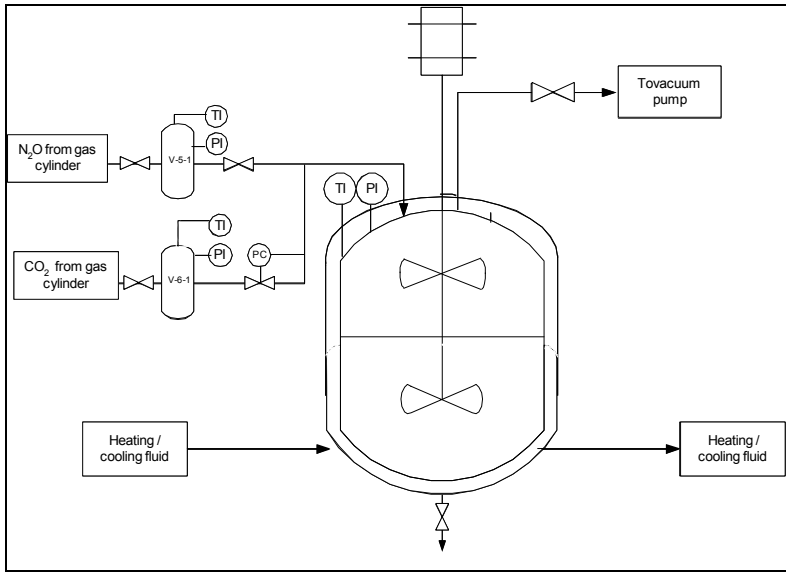


Figure 1. Schematic drawing of the experimental setup.

In a typical experiment, an ammonia solution with desired concentration was prepared from more concentrated ammonia solutions (e.g. 5.0 N and ca. 30 wt.% in water – obtained from Sigma-Aldrich) by dilution with water. Subsequently, 500 mL of the solution was transferred to the reactor, where inerts were removed by applying vacuum for a short while. Next, the solution was allowed to equilibrate at the desired temperature – and its vapor pressure was recorded. Then a predetermined amount of carbon dioxide was added from the gas supply vessel to the reactor, the stirrer was started (at about 100 rpm to ensure a flat gas-liquid contact area), and the pressure decrease was recorded with time. The actual concentration of ammonia in the solution was verified after the experiment using volumetric titration with a standard hydrochloric acid solution.

A carbon dioxide mass balance over the gas phase yields in combination with equations (6) and (7), the following equation :

$$\frac{d \ln P_{CO_2}}{dt} = \frac{\sqrt{k_{OV} D_{CO_2} A_{GL} m}}{V_G} \quad (11)$$

Hence, a plot of the natural logarithm of the CO_2 partial pressure versus the time is to yield a straight slope, from which the overall kinetic rate constant k_{OV} can be determined, once the required physico-chemical constants are known. (see also e.g. Blauwhoff et al [11] or Derks et al. [12]) The methods used to estimate the diffusion and distribution coefficient of CO_2 in aqueous ammonia are described below:

The diffusion coefficient of CO_2 is estimated from the solution's viscosity using a modified Stokes-Einstein equation:

$$D_{CO_2}^{NH_3-sol} = D_{CO_2}^{H_2O} \left(\frac{\eta^{H_2O}}{\eta^{NH_3-sol}} \right)^{0.8} \quad (13)$$

The diffusion coefficient of CO_2 in water was taken from Versteeg and Van Swaaij [13]:

$$D_{CO_2}^{H_2O} = 2.35 \cdot 10^{-6} \exp\left(\frac{-2119}{T}\right) \quad (14)$$

Viscosities of aqueous ammonia and pure water were calculated with the correlations given by Frank et al. [14]:

$$\eta^{H_2O} = 1.18 \cdot 10^{-6} \exp\left(\frac{16400}{RT}\right) \quad (15)$$

$$\eta^{NH_3-sol} = (0.67 + 0.78 \cdot x_{NH_3}) \cdot 10^{-6} \exp\left(\frac{17900}{RT}\right) \quad (16)$$

The distribution coefficient of CO₂ is estimated using the CO₂:N₂O analogy :

$$m_{CO_2}^{NH_3-sol} = m_{CO_2}^{H_2O} \left(\frac{m_{N_2O}^{NH_3-sol}}{m_{N_2O}^{H_2O}} \right) \quad (17)$$

The distribution coefficients of both CO₂ and N₂O in water were calculated using the correlations given by Jamal [15]. The physical solubility of N₂O in aqueous ammonia was experimentally determined for some experimental conditions, relevant for the present study. The experimental procedure for the experimental determination was identical to the ones described in e.g. Versteeg and Van Swaaij [13] or Derks et al. [16].

5. Results

The physical solubility of nitrous oxide in aqueous ammonia solutions was measured at temperatures between 5 and 25 °C and concentrations ranging from 0 to ca. 5 kmol m⁻³. The experimental results are shown graphically in Figure 2. From the experimental data listed in Figure 2, it can be concluded that the physical solubility of N₂O is hardly influenced by the presence of ammonia.

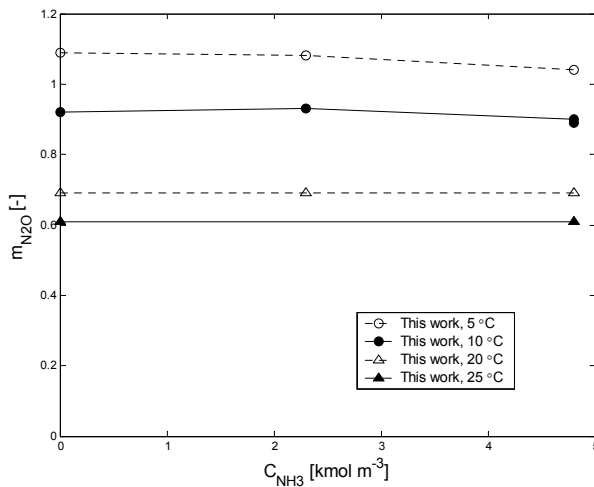


Figure 2. Physical solubility of N₂O in aqueous ammonia solutions between 5 and 25 °C.

All results on the absorption rate experiments of carbon dioxide in aqueous ammonia solutions are shown graphically in Figure 3: the apparent kinetic rate constant k_{app} is given as a function of ammonia concentration for temperatures of 5, 10, 20 and 25 °C. Also the values reported by Pinsent et al. at 10 and 20 °C are included in the graphs.

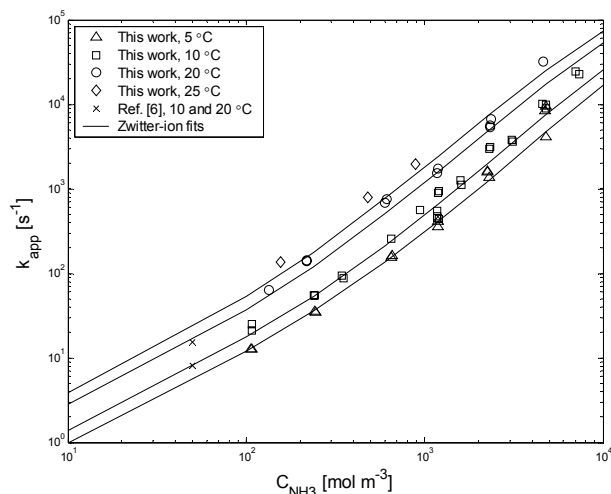


Figure 3. Experimentally determined apparent kinetic rate constants as a function of ammonia concentration.

The obtained apparent rate constants k_{app} were subsequently correlated using the previously described zwitter-ion mechanism. The individual rate constants were assumed to have the following temperature dependence::

$$k_X = k_{X-283} \exp\left(\frac{A}{283.15} - \frac{A}{T}\right)$$

The zwitterion parameters as found by fitting them to the present experimental data and the data reported by Pinsent et al. [6], are listed in Table 1. A graphical comparison between the experimental k_{app} as a function of ammonia concentration, and the curves according to the zwitter-ion mechanism, are given in Table 1:

Table 1. Kinetic parameters of the reaction between NH_2 and CO_2 according to the zwitter-ion mechanism.

	k at 283.15 K	A [K ⁻¹]
k_2	$> 7.5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$3.0 \cdot 10^3$
$k_{\text{NH}_3} \cdot k_2 / k_1$	$3.8 \cdot 10^{-4} \text{ m}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$8.5 \cdot 10^3$
$k_{\text{H}_2\text{O}} \cdot k_2 / k_1$	$2.6 \cdot 10^{-6} \text{ m}^6 \text{ mol}^{-2} \text{ s}^{-1}$	$5.5 \cdot 10^3$

A comparison between the apparent rates of reaction of carbon dioxide and ammonia, and the conventional alkanolamines monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) is given in Table 2. The comparison is made at three different concentrations, namely $C_I = 0.6 \text{ kmol m}^{-3}$; $C_{II} = 1.0 \text{ kmol m}^{-3}$ and $C_{III} = 4.5 \text{ kmol m}^{-3}$.

Table 2. Comparison of the kinetic rates of aqueous ammonia, MEA, DEA and MDEA with carbon dioxide.

	$k_{app} / 10^3 \text{ s}^{-1}$			Source
	$C = 0.6 \text{ kmol m}^{-3}$	$C = 1.0 \text{ kmol m}^{-3}$	$C = 4.5 \text{ kmol m}^{-3}$	
NH₃ @ 5 °C	0.14	0.3	8	this work
NH₃ @ 10 °C	0.21	0.7	10	this work
NH₃ @ 20 °C	0.76	1.4	30	this work
NH₃ @ 25 °C	1.0	2.1	-	this work
MEA @ 25 °C^a	3.6	6.0	27	Versteeg et al. [17]
DEA @ 25 °C	0.27	0.58	6.5	Versteeg & Oyeveaar [18]
MDEA @ 25 °C^a	$\approx 10^{-3}$	$\approx 10^{-2} - 10^{-3}$	$\approx 10^{-2}$	Versteeg et al. [17]

^a $k_{app} = k_2 \cdot C_{amine}$ in the case of MEA and MDEA

From the results in Table 2, it can be concluded that the rate of reaction of molecular ammonia with CO₂ is in the same order of magnitude as MEA or DEA (depending on the applied concentration) – and in this respect it could be an attractive solvent for CO₂ capture. However, the major disadvantage of applying such high concentrations of ammonia, is its volatility, which would require one or more washing sections to remove the ammonia from the gas leaving the top of the absorber.

6. Conclusion

The kinetics of the (carbamate formation) reaction between carbon dioxide and ammonia in aqueous solutions were determined in a stirred cell type of contactor at temperatures between 5 and 25 °C and ammonia concentrations ranging from 0.1 to about 7 kmol m⁻³. The obtained overall kinetic rate results were interpreted using the well-known zwitterion mechanism.

It was observed that the rate of the reaction between ammonia and carbon dioxide in aqueous solution is in the same order of magnitude as the conventional alkanolamines MEA and DEA – and hence substantially faster than the reaction between CO₂ and MDEA.

7. Acknowledgement

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8. References

1. E. Gal (2006). Ultra cleaning of combustion gas including the removal of CO₂. Patent Nr WO 2006/022885
2. S. Pexton and E.H.M. Badger (1938). Vapour pressures of ammonia and carbon dioxide in equilibrium with aqueous solutions. J. Chem. Ind. 57:106-113
3. F. Kurz, B. Rumpf and G. Maurer (1995). Vapor-liquid-solid equilibria in the system NH₃-CO₂-H₂O from around 310 to 470 K: New experimental data and modelling. Fluid Ph Eq. 104:261-275
4. G.R. Pazuki, H. Pahlevanzadeh and A. Mohseni Ahooei (2006). Solubility of CO₂ in aqueous ammonia solution at low temperature. Computer Coupling of Phase Diagrams and Thermochemistry 30:27-32
5. C. Faurholt (1925). Études sur les solutions aqueuses de carbamates et de carbonates. J. Chim. Phys. 22:1-44
6. B.R.W. Pinsent, L. Pearson and F.J.W. Roughton (1956). The kinetics of combination of carbon dioxide with ammonia. Trans. Far. Soc. 52:1594-1598

7. H. Bai and A.C. Yeh (1997). Removal of CO₂ greenhouse gas by ammonia scrubbing. *Ind. Eng. Chem. Res.* 36:2490-2493
8. Chilled-ammonia post combustion CO₂ capture system – Laboratory and economic evaluation results. EPRI, Palo Alto, CA (USA): 2006 1012797
9. M. Caplow. Kinetics of carbamate formation and breakdown. *J. Am. Chem. Soc.*, 90:6795–6803, 1968
10. P.V. Danckwerts. The reaction of CO₂ with ethanolamines. *Chem. Eng. Sci.*, 34:443–446, 1979
11. P.M.M. Blauwhoff, G.F. Versteeg, and W.P.M. Van Swaaij. A study on the reaction between CO₂ and alkanolamines in aqueous solutions. *Chem. Eng. Sci.*, 39:207–255, 1984
12. P.W.J. Derks, T. Kleingeld, C. van Aken, J.A. Hogendoorn and G.F. Versteeg (2006). Kinetics of absorption of carbon dioxide in aqueous piperazine solutions, *Chemical Engineering Science*, vol. 61(20), pp. 6837-6854
13. G.F. Versteeg and W.P.M. Van Swaaij. Solubility and diffusivity of acid gases (CO₂ and N₂O) in aqueous alkanolamine solutions. *J. Chem. Eng. Data*, 33:29–34, 1988
14. M.J.W. Frank, J.A.M. Kuipers and W.P.M. van Swaaij (1996). Diffusion Coefficients and Viscosities of CO₂ + H₂O, CO₂ + CH₃OH, NH₃ + H₂O, and NH₃ + CH₃OH Liquid Mixtures. *J. Chem. Eng. Data* 41:297-302
15. A. Jamal (2002). Absorption and desorption of carbon dioxide and carbon monoxide in alkanolamine systems (PhD thesis). University of British Columbia (2002)
16. P.W.J. Derks, J.A. Hogendoorn and G.F. Versteeg (2005). Solubility of N₂O in, and density, viscosity, and surface tension of aqueous piperazine solutions, *Journal of Chemical and Engineering Data*, vol. 50(6), pp. 1947-1950
17. G.F. Versteeg, L.A.J. Van Dijk, and W.P.M. Van Swaaij. On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions. An overview. *Chem. Eng. Comm.*, 144:113–158, 1996.
18. G.F. Versteeg and M.H. Oyeveaar (1989). The reaction between CO₂ and diethanolamine at 298 K. *Chem. Eng. Sci.* 44:1264-1268